PB84-122829

# Identification of Compounds in Particulate Pollution by X-Ray Diffraction

(U.S.) Naval Research Lab., Washington, DC

Prepared for

Environmental Sciences Research Lab.
Research Triangle Park, NC

Nov 83

U.S. Department of Commerce
National Technical Information Service
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**TECHNICAL REPORT DATA**
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| 1. REPORT NO. | 2. | 3. RECIPIENT'S ACCESSION NO. |
|---|---|---|
| EPA-600/3-83-107 | | PB84 122829 |

| 4. TITLE AND SUBTITLE | 5. REPORT DATE |
|---|---|
| IDENTIFICATION OF COMPOUNDS IN PARTICULATE POLLUTION BY X-RAY DIFFRACTION | November 1983 |
| | 6. PERFORMING ORGANIZATION CODE |
| 7. AUTHOR(S) | 8. PERFORMING ORGANIZATION REPORT NO. |
| J.V. Gilfrich and L.S. Birks | |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS | 10. PROGRAM ELEMENT NO. |
| Condensed Matter and Radiation Science Division<br>Naval Research Laboratory<br>Washington, D.C. 20375 | CDTA1D/01 Task 0388 (FY-83) |
| | 11. CONTRACT/GRANT NO. |
| | Interagency Agreement<br>AD-17-F-0-079-0 |
| 12. SPONSORING AGENCY NAME AND ADDRESS | 13. TYPE OF REPORT AND PERIOD COVERED |
| Environmental Sciences Research Laboratory - RTP, NC<br>Office of Research and Development<br>U.S. Environmental Protection Agency<br>Research Triangle Park, North Carolina 27711 | Final Report |
| | 14. SPONSORING AGENCY CODE |
| | EPA/600/09 |

15. SUPPLEMENTARY NOTES

16. ABSTRACT

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Four commercial diffractometers with automated "search-match" capabilities were employed to measure simulated and actual pollution particulate samples deposited on filter substrates and in bulk. These instruments are shown to be moderately efficient for the identification of mixtures of reasonably-well-crystallized compounds in the simulated samples; when averaged over all four instruments, about 60% success was achieved. While mostly poor results were realized with the actual samples, the software is still in the development stage. The tremendous potential of x-ray diffraction suggests that it should be added at this time to the stable of techniques for the characterization of pollution particulate samples.

17. KEY WORDS AND DOCUMENT ANALYSIS

| a. DESCRIPTORS | b. IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group |
|---|---|---|
| | | |

| 18. DISTRIBUTION STATEMENT | 19. SECURITY CLASS *(This Report)* | 21. NO. OF PAGES |
|---|---|---|
| RELEASE TO PUBLIC | UNCLASSIFIED | 50 |
| | 20. SECURITY CLASS *(This page)* | 22. PRICE |
| | UNCLASSIFIED | |

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

PB84-122829

EPA-600/3-83-107
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# IDENTIFICATION OF COMPOUNDS IN PARTICULATE POLLUTION BY X-RAY DIFFRACTION

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Interagency Agreement AD-17-F-0-079-0

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X-ray diffraction is a valuable tool for the identification of crystalline compounds in a multicomponent sample. Two x-ray diffraction techniques (Seeman-Bohlin and Bragg-Brentano) were examined for the identification of small amounts of material deposited on low-mass substrates. The Seeman-Bohlin focusing camera has somewhat better resolution than the Bragg-Brentano diffractometer but the commercial availability of the automated diffractometer and the sophistication of the computer programs for identifying the crystalline compounds are decisive advantages.

Four commercial diffractometers with automated "search-match" capabilities were employed to measure simulated and actual pollution particulate samples deposited on filter substrates and in bulk. These instruments are shown to be moderately efficient for the identification of mixtures of reasonably-well-crystallized compounds in the simulated samples; when averaged over all four instruments, about 60% success was achieved. While mostly poor results were realized with the actual samples, the software is still in the development stage. The tremendous potential of x-ray diffraction suggests that it should be added at this time to the stable of techniques for the characterization of pollution particulate samples.

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## ACKNOWLEDGMENTS

The authors express their appreciation to J.W. Sandelin who constructed the special Seeman-Bohlin camera and made the measurements with it in the first phase of this program.

The second phase of this project could not have been accomplished without the assistance of the X-ray manufacturers. We gratefully acknowledge their enthusiastic cooperation. Specifically, we would like to thank Dennis Ahr and Bernie Squires of Philips, Bob Myers (E.S. Industries) and Don Beard of Siemens, Jack Enderlein (International Instrument Corp.) and John Boslett of Rigaku, and Dick Hunt, Steve Neff and Joe Padur of Diano, for their considerable time and effort which made these measurements possible.

# SECTION I

## INTRODUCTION

The identification of chemical species present in particulate pollution is an important facet of the overall problem of specifying probable sources and developing effective control technology. While x-ray fluorescence (XRF) has been shown to be an appropriate technique for the elemental analysis of both ambient and emission source samples,[1,2] and valence band x-ray spectroscopy readily distinguishes between the sulfide and sulfate forms of sulfur,[3] a general technique for the identification of the compounds present in such samples has not been available.

X-ray diffraction (XRD) has been used as a routine method for the qualitative (and in some cases quantitive) analysis of the compounds present in bulk samples for many years.[4] More recently the problems associated with free silica in the work space atmosphere have been attacked quite successfully by this technique.[5] However, the use of XRD as a tool for the routine characterization of particulate pollutants has received minimal attention,[6] in one case suggesting 24 hour runs.[7]

The present study has examined the problem from two aspects. In the first phase, laboratory experiments were conducted to compare two types of x-ray optics [Seeman-Bohlin(S-B) and Bragg-Brentano (B-B)] useful for determining the compounds present in parti-

culate pollution samples collected on thin substrates. The second phase evaluated commercial automated B-B XRD instruments equipped with "search-match" facilities to provide computer-identification of the compounds present. Both phases of this work used simulated samples in which mixtures of known compounds were deposited on thin substrates to test the success of identification. In addition the second phase examined some bulk samples and some actual pollution samples collected from emission sources.

## SECTION 2

## CONCLUSIONS

The results of the first phase of this investigation showed that the focusing of the diffracted beam provided by the curved sample in the S-B camera achieved somewhat better resolution than the B-B diffractometer which uses a flat sample. The use of photographic film in commercial S-B instruments is inconvenient and certainly mitigates against automation. Thus, in spite of slightly poorer resolution, the B-B diffractometer maintains its position as the instrument of choice because of adequate resolution, commercial availability of models using electronic detection systems and the higher efficiency of the automated versions.

In the second phase of this work, the automated B-B instruments marketed by four x-ray manufacturers (Philips, Siemens, Rigaku and Diano - listed in the order by which their applications laboratories were visited) were evaluated and compared with measurements made on the same set of samples at the Naval Research Laboratory (NRL) using a manual instrument (vintage 1950, Philips), while some of the data from the first phase was interpreted "off-line" by a "search-match" program on an external computer.

All four of the automated diffractometers operated very well, as would be expected since they are essentially the same instruments as have been used in the community for many years; the automation

simply removes much of the tedium of running the diffraction patterns and reducing the data. The different manufacturers implement the "search-match" capability in different ways. The one striking similarity among them is the state of flux of the computer software. The prototype versions of the computer programs are being changed frequently, with updates provided for the user periodically. The end result of this development is that no conclusion can be reached concerning the ultimate efficiency of the various "search-match" techniques relative to one another because none are in final form. It is true, however, that at the time on these measurements, some routines seemed to work better than others in particular ways, but that no one of them was completely satisfactory. It is interesting to compare the result of this exercise with reports in the literature[8,9,10] of roundrobin tests of x-ray diffraction on bulk mixtures of compounds. These round-robin tests concerned themselves with both automated (off-line) and manual data reduction but did not include the specific computer programs being used with the automated instruments. Generally speaking the results reported in these references were very good, but the comment was made that the participants in the tests represented the "upper-crust" of the x-ray diffraction world and that it would be expected that routine x-ray diffraction data collected in the average laboratory would be significantly lower in quality than that leading to the excellent results reported for these round-robins. It must be recognized also, that with

both manual data interpretation and that which uses an off-line computer program, considerable "human" decision-making is involved. For the diffractionists who fit the "upper-crust" characterization, this leads to improved results. For the programs built in to the automated instruments, such interactive operation is also possible, but the tendency of the operator is to let the computer do as much as possible, always a problem with any automated device. The results of the exercise conducted at the applications laboratories showed about 60% success when averaged over all four. No one instrument succeeded in unequivocally identifying all three simulated samples on filters. And only two of the instruments identified all four compounds in the undiluted bulk sample.

All of the instruments collected diffraction patterns which looked reasonable on a strip chart or video terminal, and were interpretable, for most of the samples in 20 to 40 minutes. The results on the simulated samples (described above) showed some success but the actual pollution samples pose a much more difficult problem. Many of the compounds present may be poorly crystallized and therefore give inadequate diffraction patterns; also they may have large amorphous fractions (e.g. carbon present as soot) causing a high background which makes recognition of those peaks which are present more difficult. It may also be possible that compounds present in actual samples may not be included in the data base.

## SECTION 3

## RECOMMENDATIONS

### USE OF AUTOMATED DIFFRACTOMETERS

Much work is yet to be done before x-ray diffraction is ready to be used in the characterization of particulate pollutants on a routine basis. The state-of-the-art of the modern automated diffractometer is such that it should be added to the stable of instruments invoked to attack the problem. The "search-match" program with which such an instrument may be equipped must be used with some care, recognizing that it has limitations. In fact, it would be desirable to also have an "off-line" computer program through which the data might be run for redundancy (assuming that the raw data can be retrieved from the automated instrument). One such program, available from a commercial time-sharing service for those laboratories without the facilities to set up one of the other programs is available from Interactive Sciences Corporation, which implements the NIH/EPA Chemical Information System (CIS). As progress is made in software development on the automated instruments, the power of their respective "search-match" routines may improve and do away with the necessity for the "off-line" program.

### SAMPLE HOLDER

None of the commercial instruments had sample holders which were ideally suited for the filter samples. Most used adaptations

of the standard bulk sample holder with the filter mounted on the surface of the flat plate and the cavity conventionally used to contain the bulk powder behind the filter. The most appropriate sample holder was used at Siemens where a United Stated Steel Corporation design was available. This holder was designed to contain a 25mm silver filter for the determination of free silica in airborne dust and to be handled by an automatic sample changer. An exploded sketch of this device is shown in Figure 1. For our purposes the holder was used without the steel disk (to decrease the background); the snap-ring held the 25mm filter flat enough for adequate diffraction patterns. An adaptation of this type of sample holder could be, and should be, used with any of the commercial instruments, although it would be better to have it hold larger filters (37 or 47mm). A filter holder usuable in both x-ray fluorescence and x-ray diffraction equipment would be a great convenience.

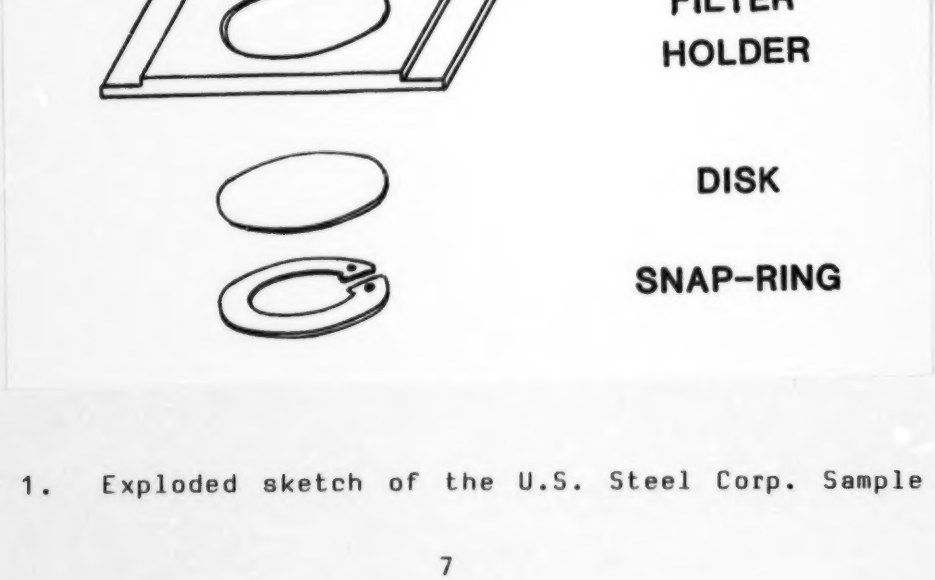



Figure 1. Exploded sketch of the U.S. Steel Corp. Sample Holder.

## SECTION 4

## PHASE I

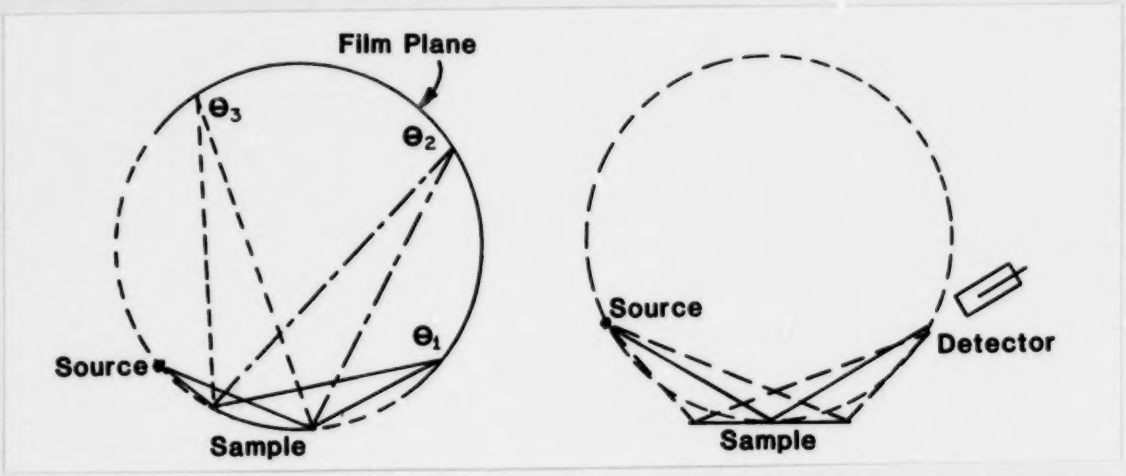
### SAMPLES

For the initial work samples were prepared by dusting powdered compounds onto pressure-sensitive transparent tape over a defined area. The tape was weighed before and after deposition of the sample; about 1 $mg/cm^2$ was the minimum deposit which could be prepared with any certainty. The tape was mounted first on the arc of the S-B camera for exposure and subsquently on a flat holder for the B-B diffractometer. Samples prepared in this fashion included $(NH_4)_2SO_4$, $CaCO_3$, $Na_2SO_4$ and $Na_2SO_3$ individually, and binary mixtures of $(NH_4)_2SO_4$ and $CaCO_3$, and $Na_2SO_4$ and $Na_2SO_3$.

### EXPERIMENTAL

The S-B camera uses a curved sample which focusses the diffracted x-rays to the film plane, the instrumental broadening of the diffraction peak being controlled by the size of the source. Commercial S-B cameras are available only using a slit as a virtual source. The distance of the slit from the x-ray tube focal spot and thus the solid angle subtended limits the intensity drastically. Such a camera was employed in our first measurements but no diffraction pattern was observed from microsamples even after an hour's exposure.

A laboratory model S-B camera was constructed which used the line source of a standard x-ray tube. (It will be remembered that the line source is used with the B-B diffractometer; the laboratory S-B camera also required soller slits similar to those used in the diffractometer to minimize the sideways fanning of the incident and diffracted beam). This camera was designed with a large focussing circle (18", 46 cm) in order to simplify recording the low angle diffraction pattern on film while shielding the film from the direct beam. The S-B data discussed below was obtained with this camera which produced acceptable exposures in 10 to 20 minutes with the Ni-filtered Cu x-ray tube operated at 45 kV, 10 mA. The S-B camera is illustrated in Figure 2a.




a. Seeman-Bohlin Camera b. Bragg-Brentano Diffractometer

Figure 2. Geometry for two x-ray diffraction optics.

The B-B diffractometer is the instrument most often used to obtain powder diffraction patterns. Over more than 30 years, it has been developed into a very useful device. The measurements reported here used a Cu-target diffraction tube with a Ni $K\beta$ filter, again at 45 kV and 10 mA, using 1° divergence slits, a 0.006 inch (0.15mm)

receiving slit and scintillation counter with pulse height selection. The scanning rate was 2° 2θ per minute so that 10° to 50° required 20 minutes. The flat sample used by the diffractomter is a disadvantage because the diffraction peak is broadened due to the ends of the sample falling off the focussing circle. This is illustrated by the dashed lines in Figure 2b.

In both the B-B diffractometer and the S-B camera, the sample was supported by a holder having a hole located so the direct beam would not be diffracted or scattered by the mount materials.

RESULTS AND DISCUSSION

Figures 3 a.-c. show portions of the diffraction patterns for two of the compounds individually and a mixture of those two compounds. In each case a densitometer trace of the S-B film is the upper trace, overlaid with a print of the film itself; the lower curve is the diffractometer record of the same sample but on a flat holder rather than the curved holder of the S-B camera. The compounds are easily distinquished from one another with either instrument. Slightly better resolution with the S-B camera is illustrated by the close doublet labelled A in Figure 3c.

Sensitivity was determined with the diffractometer using a sample of 1 mg/cm$^2$ $CaCO_3$ and measuring the strongest line, d=3.03 Å. At the peak of the line there were 540 cps above a background of 40 cps for a sensitivity of 500 counts per second/mg per cm$^2$. Limit of detection calculated using the 3$\sigma$ definition as in XRF is $C_L$=4 $\mu g/cm_2$ for 100 sec. counting interval. The same caveats apply as in XRF, i.e., one must be looking for the specific material and there

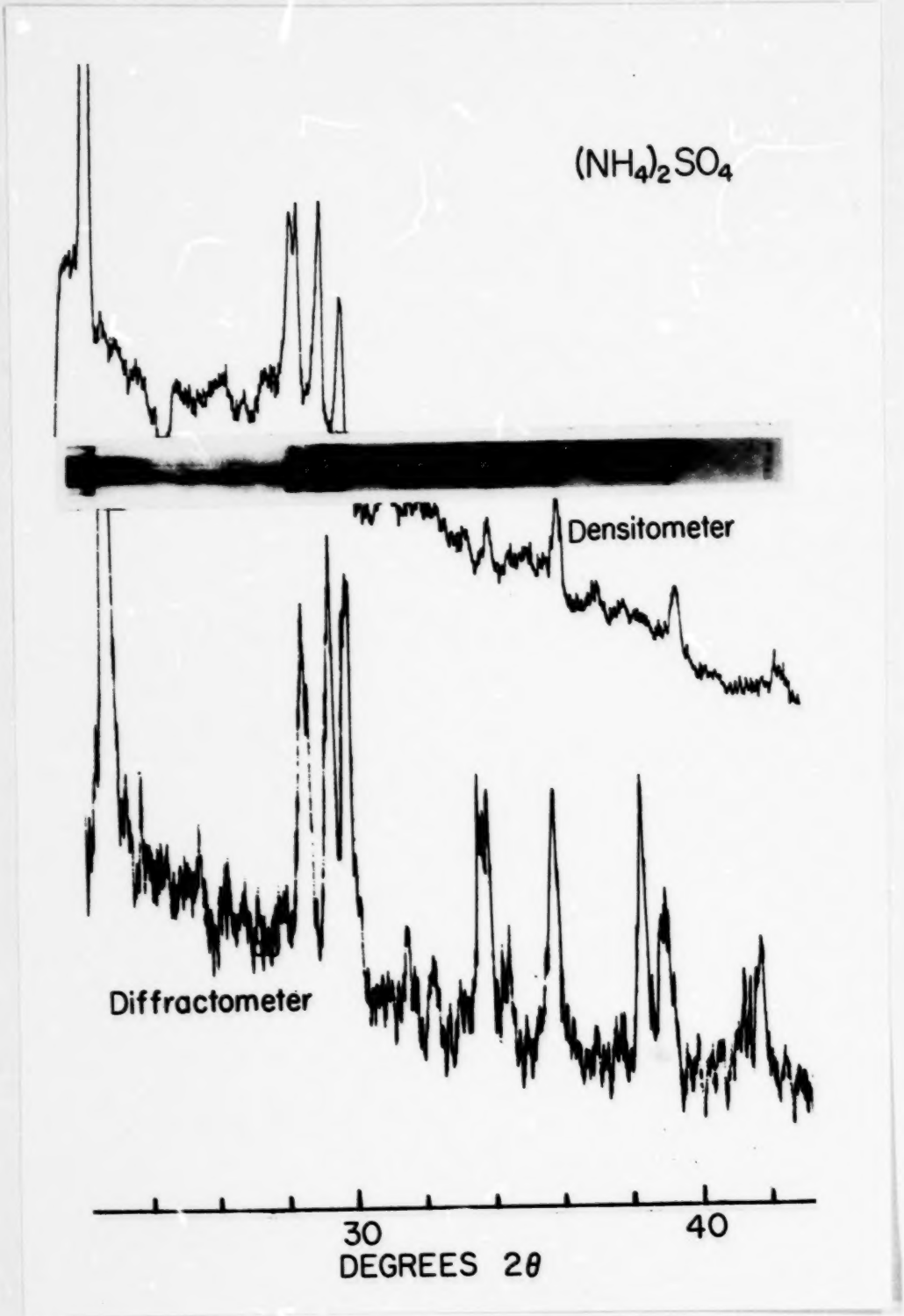



Figure 3a. Seeman-Bohlin film and its densitometer trace, and diffractometer recording of $(NH_4)_2SO_4$.

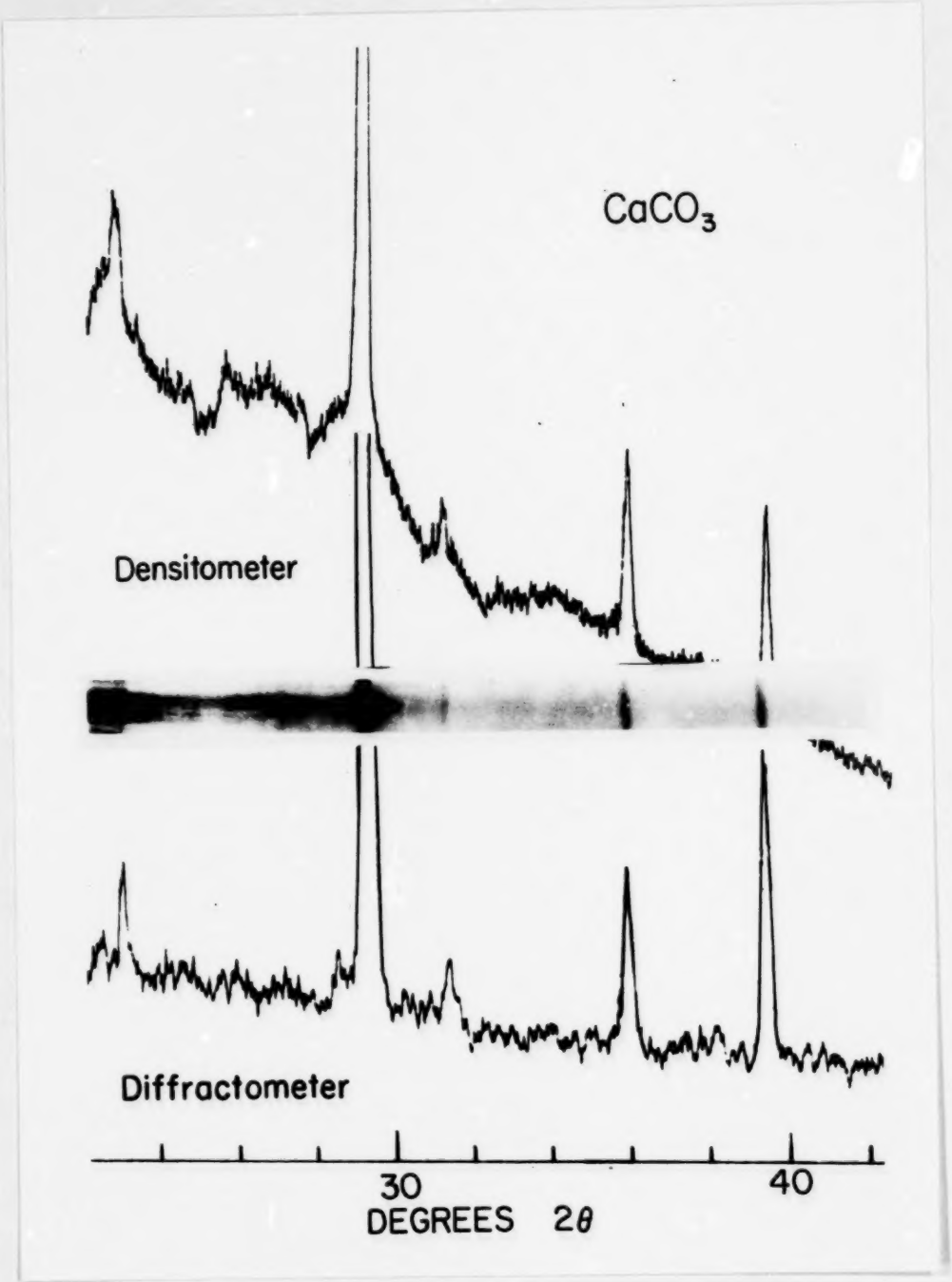



Figure 3b. Seeman-Bohlin film and its densitometer trace, and diffractometer recording of $CaCO_3$.

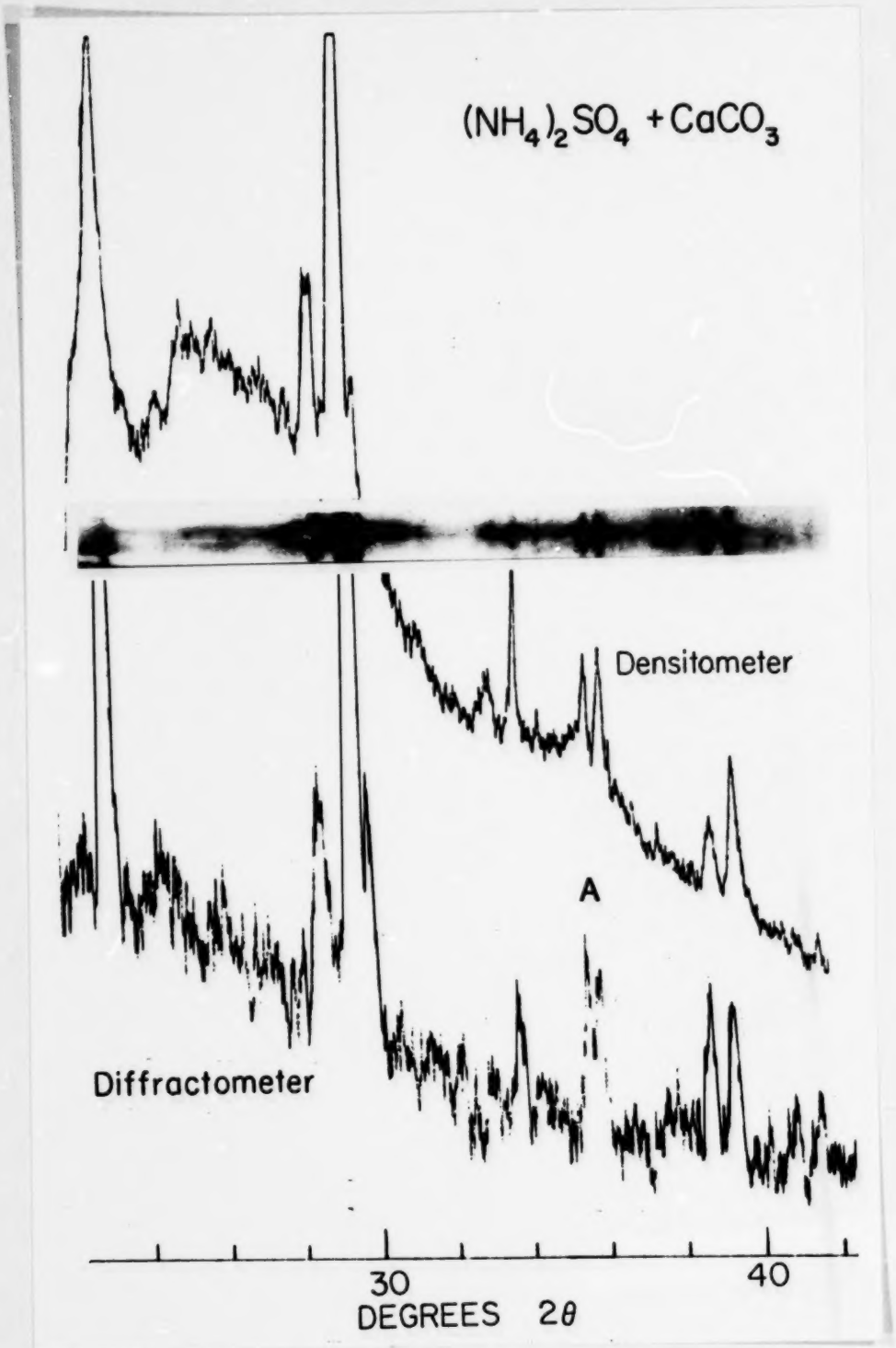



Figure 3c. Seeman-Bohlin film and its densitometer trace, and diffractometer recording of a mixture of $(NH_4)_2SO_4$ and $CaCO_3$.

must be no interfering lines. Line interference seems more likely in diffraction analysis because there are many d-spacings for each compound and many more compounds than elements. For the more likely situation where the compounds are unknown and a qualitative identification is the first step, the detection limit is degraded by perhaps several times because one needs a number of lines to be detectable to be able to match a Joint Committee for Powder Diffraction Standards (JCPDS) card. The lower intensity lines needed are frequently only 10 or 20% of the strongest line intensity. Further degradation of the detection limit is possible due to poor crystallinity.

Preferred orientation of the crystallities is a possibility which must also be considered in diffraction. For instance, when $Na_2SO_4$ powder was prepared by grinding, the d=3.08 Å line was stronger than the d=2.78 Å line which is the inverse of the relative intensities given on the JCPDS card. While it may be unlikely that actual pollution samples will show preferred orientation the fact that it can cause difficulty must not be forgotten, particularly for the "search-match" situation where relative intensities of the lines are part of the matching operation.

DATA INTERPRETATION

In the initial stages of the first phase, data interpretation was strictly manual. That is, the strip chart from the diffractometer or the densitometer tracing of the film from the S-B camera was reduced to a table of d-values and relative intensities to be compared against the diffraction data on the JCPDS card for the parti-

cular compound or compounds. Because the compounds being used were known (at this point no attempt was made to conduct "blind" tests) this was a fairly straightforward procedure. Although the relative intensities recorded by the two instruments were somewhat different (and were expected to be because of different geometry), the limited range of angles examined minimized the differences so that there was no difficulty encountered.

Recognizing that an actual unknown sample might have many compounds, producing a complicated pattern which would be difficult to interpret manually, the diffractometer data for the two samples each containing two compounds were treated by two different computer programs called "search-match". These programs "search" the JCPDS data base of almost 30,000 diffraction patterns and attempt to "match" the experimental pattern. This exercise was conducted through the good offices of Dr. C. Hubbard at the National Bureau of Standards where two of these programs ("Johnson" named after the author, and the Chemical Information System on a commercial time-sharing service) are in operation. Both programs were run successfully, unequivocally identifying both compounds present in each of the two samples as the two leading candidates.

SECTION 5

PHASE II

SAMPLES

Because the Phase I work presented data obtained on rather poorly characterized samples (one or two compounds dusted onto scotch tape), some well-characterized samples were prepared at the Enviromental Sciences Research Laboratory (ESRL) by depositing particles from an aerosol generator onto Millipore filters. Three different sets of two compounds each were prepared at different mass-loadings. Table 1 lists the starting materials and the mass-loading for each sample as determined gravimetrically. XRF analysis was performed on one sample out of each set to confirm the gravimetric values. Agreement was about 10%.

TABLE 1. AEROSOL-GENERATOR-PRODUCED DIFFRACTION SAMPLES

| | | Total Mass Loading ($\mu g/cm^2$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Set | Compounds | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| A | $KBr-K_2SO_4$ | 188 | 214 | 218 | 42 | 45 | 21 | - | - |
| B | $KCl-(NH_4)_2SO_4$ | 6304 | 2500 | 277 | 415 | 182 | - | 74 | 65 |
| C | $MgSO_4-Na_2SO_4$ | 409 | 129 | 232 | 407 | 194 | 673 | 565 | 850 |

For the continuation of Phase II some samples in addition to the ones listed in Table 1 were prepared at NRL from four reagent chemicals and starch as indicated in Table 2. A few real samples

were included to further examine capabilities. The qualitative elemental composition was determined by XRF as shown in Table 3.

TABLE 2. SIMULATED BULK POLLUTION PARTICULATE SAMPLES

| | COMPOSITION (%) | | | | |
|---|---|---|---|---|---|
| Sample | $CaCO_3$ | $Al_2O_3$ | $TiO_2$ | $Fe_2O_3$ | Starch |
| Mix I | 3.4 | 3.2 | 2.6 | 2.6 | 88.2 |
| Mix II | 14.1 | 13.3 | 9.4 | 14.4 | 48.8 |
| Mix III | 24.8 | 25.7 | 27.4 | 22.1 | ---- |

TABLE 3. ACTUAL POLLUTION PARTICULATE SAMPLES

From Lead Smelter (on Millipore Fliters)

| Sample No. | SJA-15 | SJ-16 | SJA-16 |
|---|---|---|---|
| Mass Loading ($\mu g/cm^2$) | 383 | 27 | 226 |

Elemental Analysis (All 3) : Major-Pb; Minor-S, Cl, K

From Zinc Smelter (on Millipore Filters)

| Sample No. | NZC-5 | NZC-10 | NZC-45 |
|---|---|---|---|
| Mass Loading ($\mu g/cm^2$) | 172 | 655 | 574 |

Elemental Analysis (All 3): Major-S; Minor-Ca

Fly Ash from Coal-Fired Power Plant (Bulk)

Elemental Analysis: Major-Al, Si, S, Fe; Minor-K, Ca, Ti

The bulk samples were powers contained in vials; all of the commerical instruments had samples holders designed specifically to handle that type of sample. The filter collections were on 47mm Millpore filters. None of the commerical instruments were equipped to accomodate that size although the NRL instruments was.

The Philips instrument had basic sample holders which would accomodate 37mm filters and the Siemens filter holder was 25mm in diameter. "Cookie-cutters" of the appropriate size were fabricated so that the 47mm filters could be cut to 37mm for the visit to Philips and then cut to 25mm for Siemens. Makeshift arrangements then permitted the 25mm samples to be run on the Rigaku and Diano instruments.

EXPERIMENTAL

A representative set of samples from the above were measured on the manual diffractometer at NRL with the data reduced by hand. A set of samples (not necessarily the same as at NRL) was then taken to each of the four x-ray equipment manufacturers to run on their automated diffractometers equipped with "search-match" capabilities. Table 4 details the experimental conditions for five diffractometers.

TABLE 4. DIFFRACTOMETER OPERATING CONDITIONS

| | NRL | Philips | Siemens | Rigaku | Diano |
|---|---|---|---|---|---|
| X-ray Tube Target | Cu | Cu | Cu | Cu | Cu |
| kV | 45 | 45 | 50 | 35 | 40 |
| mA | 10 | 40 | 30 | 35 | 25 |
| Scan | Cont. | Step | Step | Step | Cont. |
| Speed | 1/2°/mm | | | | 2°/min. |
| Step Size | | .02° | .02° | .02° | |
| Count Time | | 1 sec. | 0.5-1 sec. | 0.4 sec. | |
| Divergence | 1° | $\theta$ Comp. | 1° | 1° | 1° |
| Rec. Slit* | 0.15mm | 0.15mm | 0.05° | 0.15mm | 0.05° |
| Monochrom. | $\beta$ Filter | Graphite | Graphite | Graphite | Graphite |
| Detector | Scint. Cntr. | S.C. | S.C. | S.C. | S.C. |

*0.05° ≈ 0.15mm

In all cases the operator in the manufacturer's Applications Laboratory was not told what compounds were present in the known samples but only a qualitative elemental composition (determined by XRF, as might be done in actual practice.) He was then allowed to choose his experimental conditions as he saw fit, based on his experience with the instrument. Some difficulties were experienced with instrument operation, the computer manipulation of data and obtaining hard copy of the results, but none of these problems were extensive nor did they interfere with the general objectives of the exercise.

## RESULTS AND DISCUSSION

### NRL Measurements

The first step after receiving the samples prepared using the aerosol generator at ESRL was to run a selection from all the samples (Table 1, 2 and 3) at NRL and attempt to identify them from a manual search of the JCPDS data base. Samples A-1, -2 and -3 (Table 1) all with total loading of near 200 $\mu g/cm_2$ were readily identified as KBr and $K_2SO_4$, as expected. Sample A-5, at 45 $\mu g/cm_2$, gave a poor pattern with only the stronger peaks observable, too few in fact for unambiguous identification. Figure 4 shows A-3. Sample B-4 at 415 $\mu g/cm^2$ gave a good diffraction pattern which could not be identified as the starting materials KCl-$(NH_4)_2SO_4$. A manual search of the JCPDS file identified this sample as $NH_4Cl$ and $K_2SO_4$. Since all these samples were prepared from an aqueous solution of the starting salts, this was an unexpected but not unreasonable result. Samples B-3 and B-5, at 277 and 182 $\mu g/cm^2$

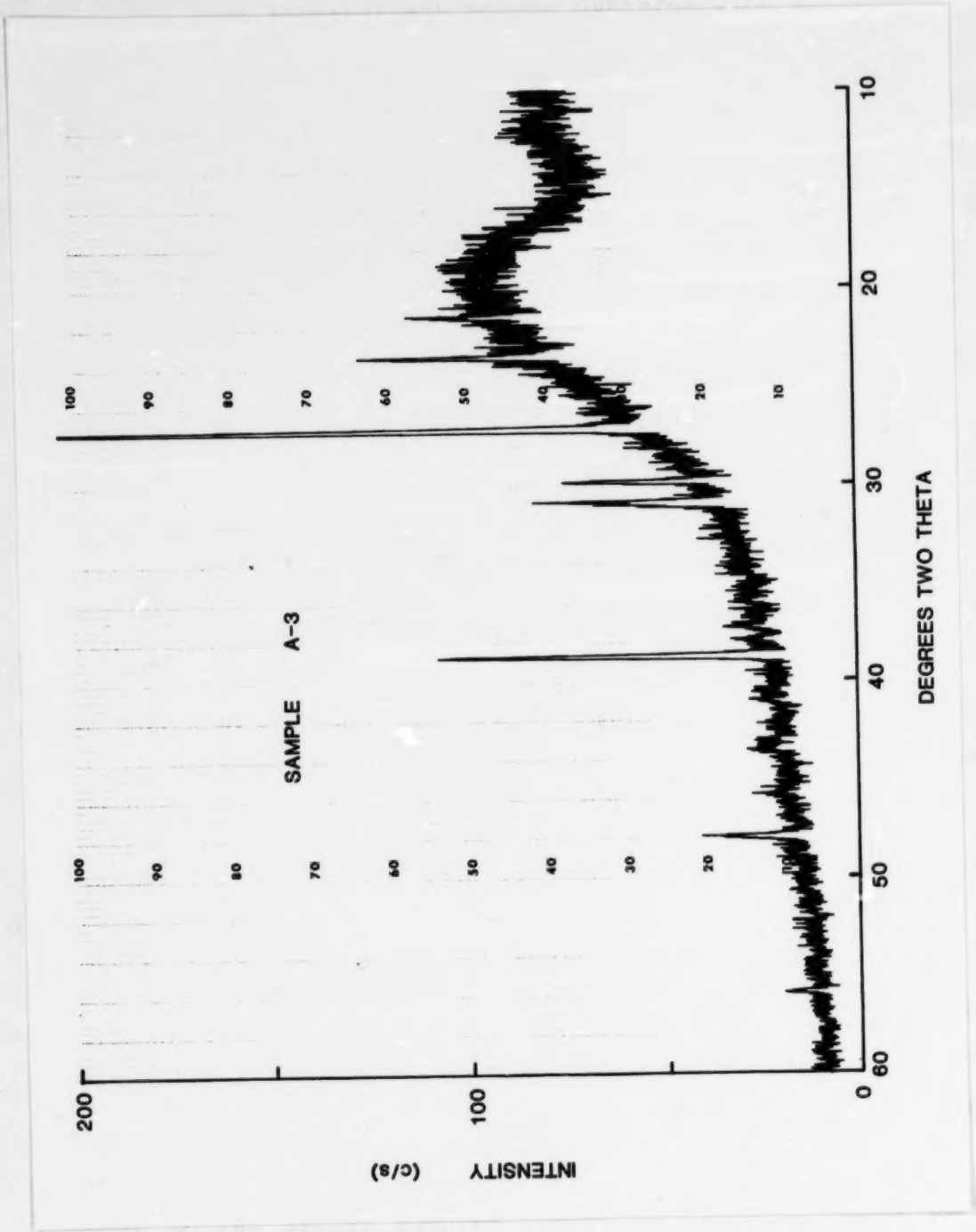



Figure 4. NRL pattern of sample A-3

respectively, gave successively poorer patterns with B-5 only marginally identifiable. Sample B-1 at fairly gross loading, 6300 $\mu g/cm^2$, gave a pattern which looked qualitatively like that which would be obtained from a bulk sample, the amorphous peak from the Millipore filter being virtually non-existent. This pattern also contained two peaks tentatively identified as residual KCl. Figure 5 and 6 show respectively, samples B-4 and B-1. Samples C-6 (Figure 7) and C-8 both gave good diffraction patterns but could not be identified as $MgSO_4$, $Na_2SO_4$ or any of their hydrates which were contained in the JCPDS file available. The pattern from C-5 contained too few peaks to consider trying to identify; those peaks which were present were consistent with the patterns from C-6 and C-8.

The simulated bulk samples were made up from reagent chemicals which gave mostly only fair diffraction patterns when run idividually. Mix III, shown in Figure 8, produced an adequate pattern to identify all four components. In order to simulate a bulk pollution sample with a considerable amount of amorphous material, Mix II and Mix I were prepared with starch as a diluent. Mix I containing about 3% of each crystalline component was only marginally identifiable, and that perhaps only because the compounds were known in advance. This was intended in the design of the exercise because it was expected that the newer instruments would have better sensitivity and should obtain better patterns at lower concentrations than achievable at NRL.

None of the actual samples listed in Table III gave patterns which could be identified satisfactorily. Both SJA-15 and NZC-10

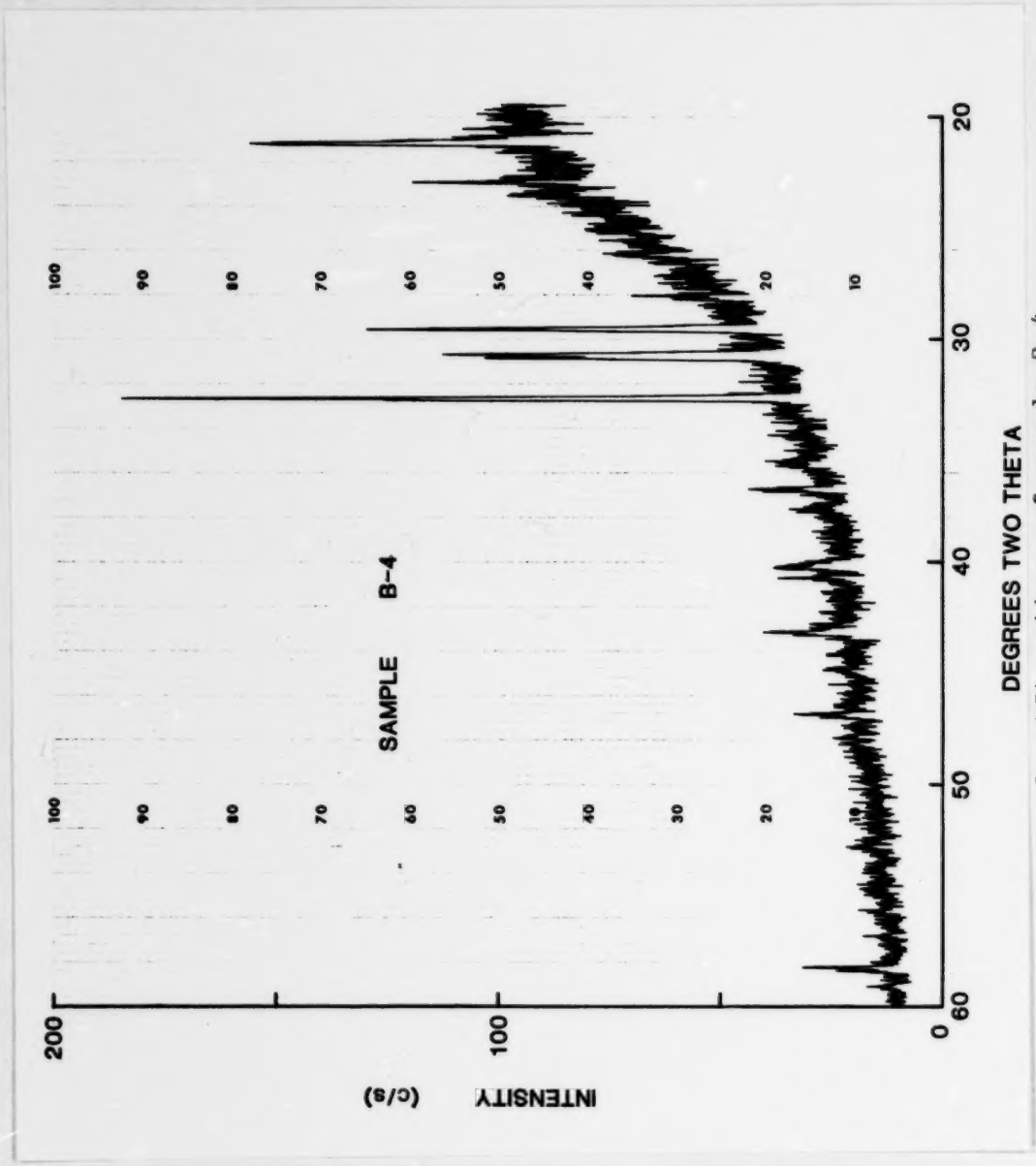



Figure 5. NRL pattern of sample B-4

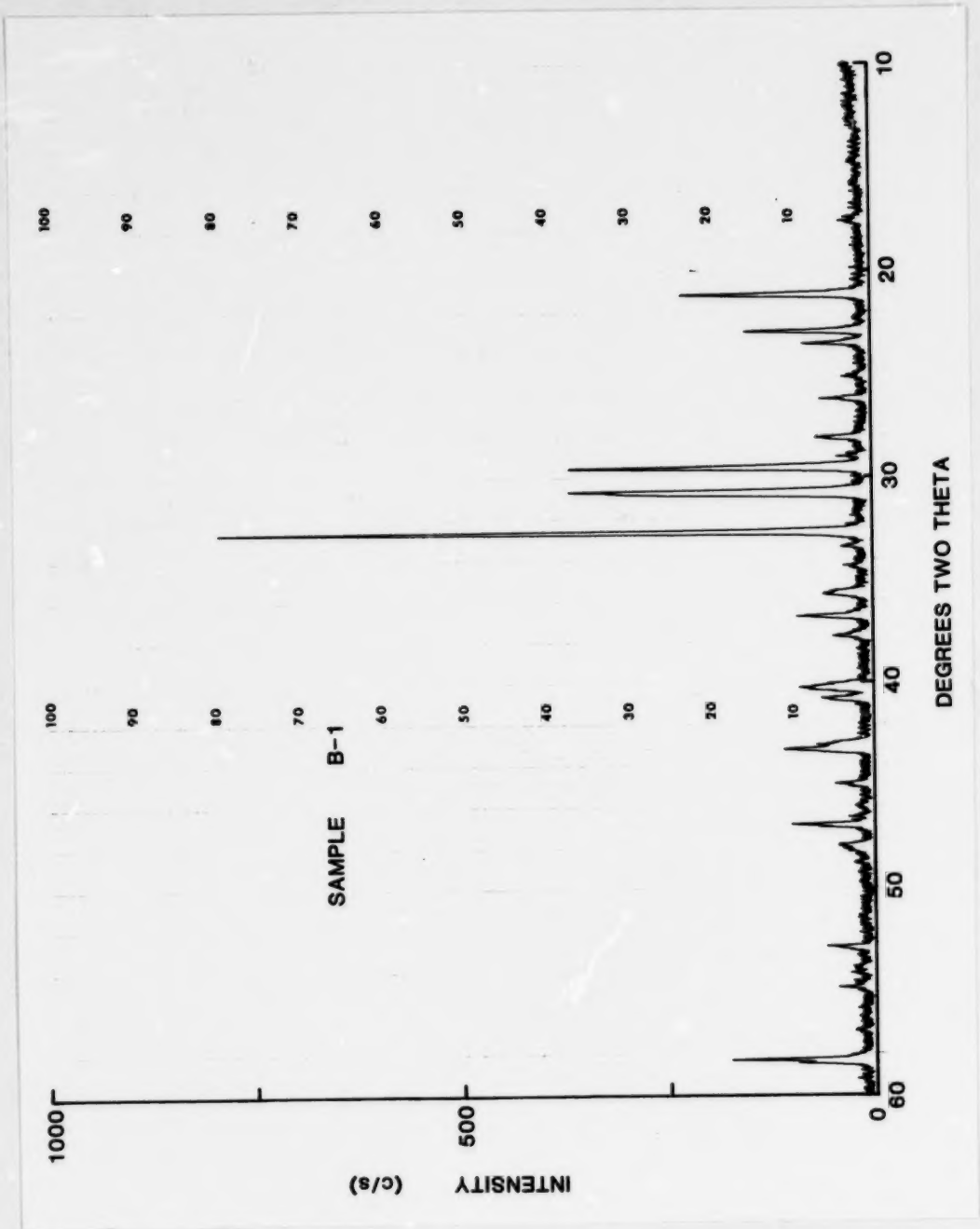



Figure 6. NRL pattern of sample B-1

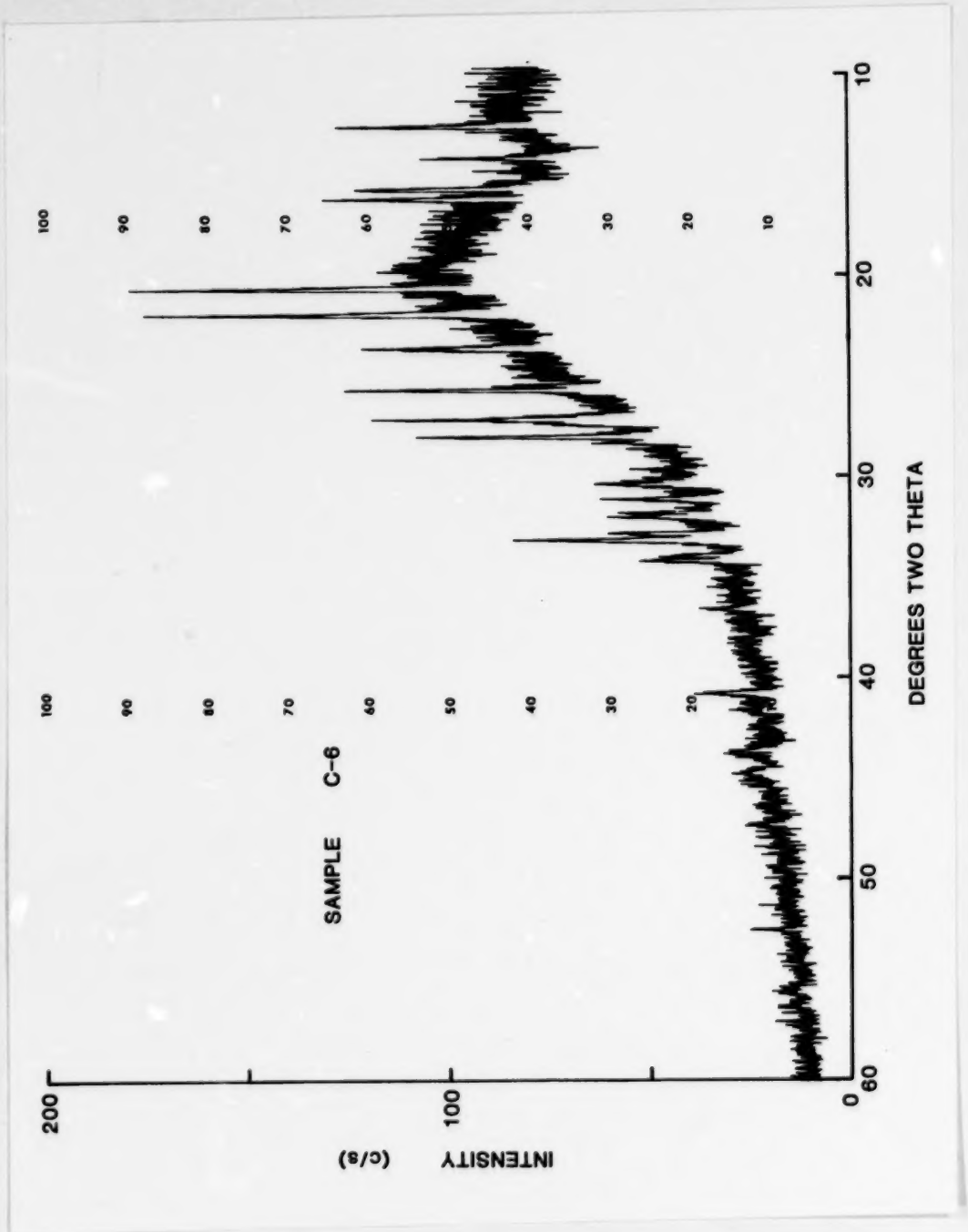



Figure 7. NRL pattern of sample C-6

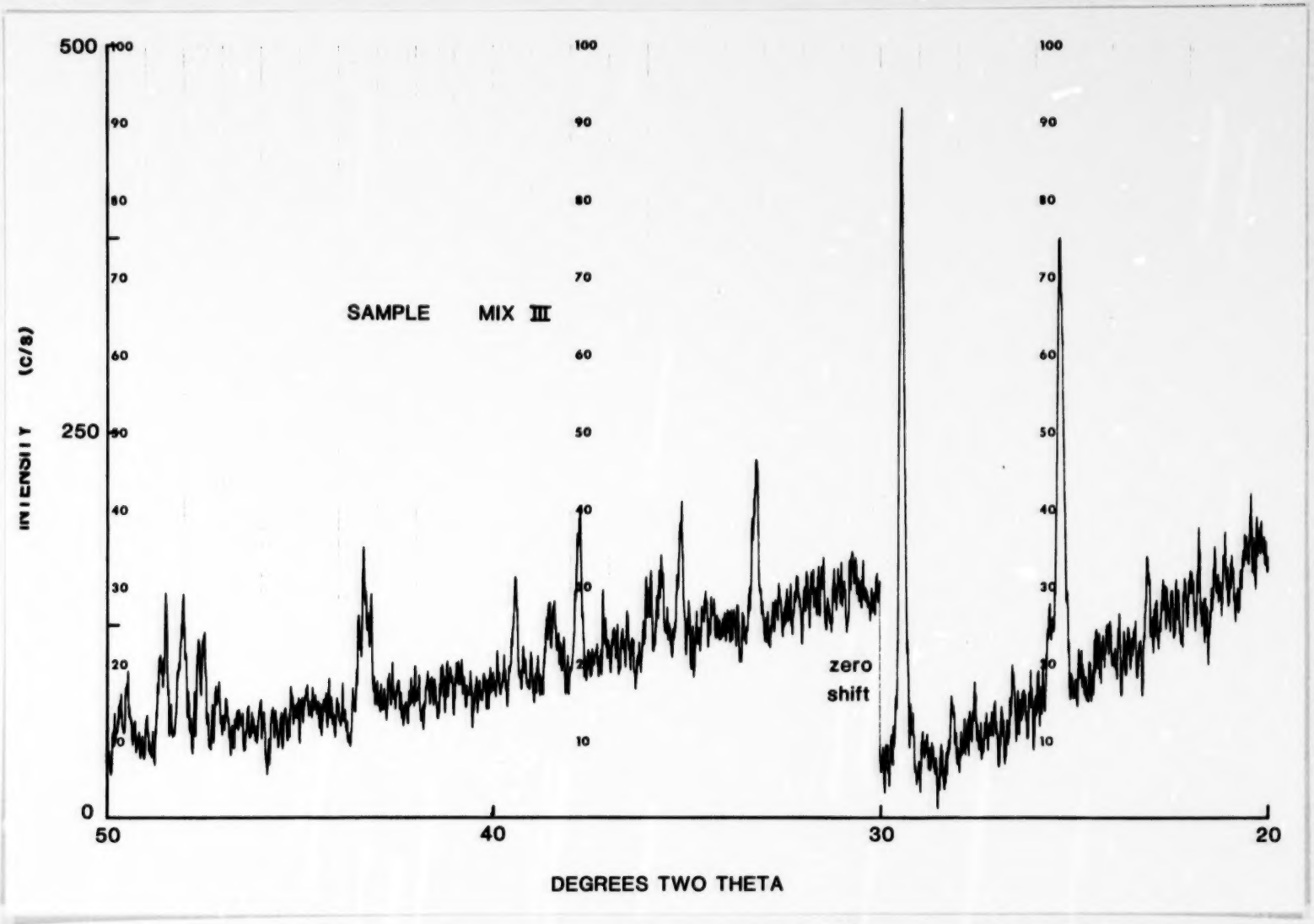



Figure 8. NRL pattern of Mix III

gave what appeared to be adequate patterns but could not be matched to any of the JCPDS file cards. NZC-10 showed some similarity to the pattern for $(NH_4)_2SO_4$ but the match was poor. Sample SJA-15 had relatively broad peaks which could not be matched at all. Figure 9 shows the pattern from NZC-10. The bulk Fly Ash sample gave a fair diffraction pattern with a large low-angle broad hump indicating significant amorphous material. It could not be identified.

Applications Laboratory Measurements

Visits of somewhat less than two days each were made to the x-ray manufacturers' application laboratories over a period of about a month and a half. Generally speaking all of the instruments performed better than the NRL diffractometer, largely because the use of higher-powered tubes provided greater intensities. The "search-match" computer programs were relatively easy to use and because most instruments were controlled and data was collected by a microprocessor system, the computer could be used for manipulation of a set of data and subjecting it to the "search-match" procedure while the instrument was running the next diffraction pattern. The amount of data that was collected in less than two days at each applications laboratory was very large; all of it cannot be included in this report. Instead, selected samples run on the different instruments will be compared with each other and with the NRL measurements, and the results of the automated search-match procedures will be illustrated.

From Set A (Table 1) sample A-2 was run at Philips, Siemens

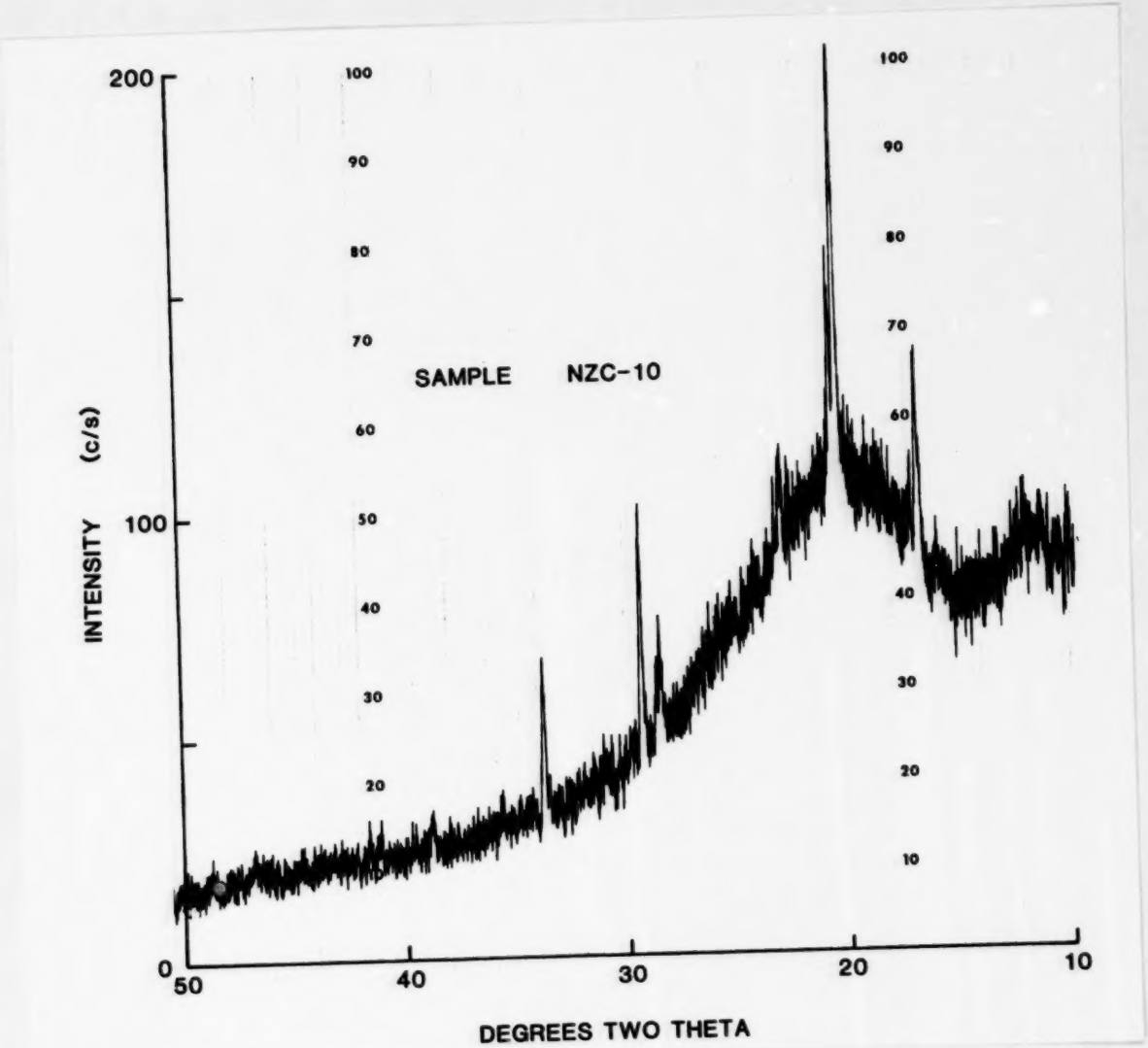



Figure 9. NRL pattern of NZC-10

and Diano. Sample A-2 was then sent to Rigaku to be run later. At Philips $K_2SO_4$ and KBr were identified as present in A-2 as shown in the printout (Figure 10). The Siemens instrument found only KBr on the first pass. Searching the residual pattern was unsuccessful. However, by subtracting the pattern for KBr manually and entering the lines and relative intensities left, $K_2SO_4$ was found. This was a curious result since the pattern seems to be adequate (Fig. 11; compare with Fig. 4) and no explanation could be uncovered. Diano succeeded in finding both compounds among more than 25 possibilities. Diano recommended not entering the elemental information and the output was much longer. The Diano output also listed the output in numerical order (by JCPDS card number) which seems a little awkward. The Diano pattern is shown in Figure 12. Rigaku ran A-2 after the visit using the rotating anode tube at 50 kV,200mA (see the discussion of the rotating anode tube later.) Both KBr and $K_2SO_4$ were found among the 8 compounds with highest reliability factors.

Sample B-4 was run unsuccessfully at Philips, not just from the "search-match" standpoint but because virtually no pattern could be discerned except for Al peaks from the sample holder. This is difficult to understand since the sample gave a reasonable pattern at NRL before going to Philips (Figure 5) and again after returning to NRL. This run also underscored the need for an appropriate sample holder since the Al lines (from the preferentially oriented Al plate) although they did not present a problem, were an undersirable artifact. The opening in the plate was the same size as the x-ray beam and the holder could not be positioned accura-

SANDMAN: MATCH SCORE TABLE - REV 1.00 2/9/81 13:44: 1
F2A.D1

SAMPLE ID: F2A MAJOR PHASE SEARCH
SCAN NUMBER
16 USER LINES 8.8370 D 1.5400 BKGND = 9.5
SCAN PARAM: 45 KV 40 MA 10.00 - 60.00 DEG 0.02 STEP 1.0 SEC/STEP
16 LINES SEARCHED WITH I 3.2 42 SEC SEARCH, 8 SEC MATCH
25867 INITIAL PATTERNS 797 INSPECTED 16 SCORED
2 PHASES IDENTIFIED AVE(EQ.D.E.) = 585 MICRONS SCORE = 8.4
MATCH SCORE TABLE CONTAINS TOP 15 ENTRIES OF 15 ABOVE SEARCH CUTOFF

| | MLMS | AMS | HT/MS/BK/UM | EQ.D.E. | I% | JCPDS# | DM | FORMULA |
|---|---|---|---|---|---|---|---|---|
| 1 | 4.3 | 3.2 | 10 0 28 1 | 525 | 33 + | 5- 613 | *M | K2 S O4 |
| 2 | 4.0 | -1.1 | 9 0 32 18 | 495 | 30 | 24- 703 | CM | K2 S O4 |
| 3 | 3.2 | 4.2 | 6 0 0 10 | 645 | 68 + | 4- 531 | *I | K BR |
| 8 | 0.2 | 1.0 | 2 0 0 8 | 420 | 59 | 9- 340 | *I | ( LI H) |

LEGEND

EQ.D.E. - Equivalent Displacement Error; Estimated deviation from focusing circle.
MLMS - Most Likely Matching Score. (Values from -25.5 to +25.5).
AMS - Additive Matching Score. (Negative value means not likely).
HT - Hit. (Number of peaks identified).
MS - Miss. (Number of peaks missed).
BK - Background. (Number of peaks falling below value selected as the background).
UM - Unmatched Peaks. (Mostly outside the 2θ range chosen).
DM - Two parameters characterizing the JCPDS pattern:
First Symbol - Quality: * - High; C - Calculated; I - Indexed.
Second Symbol - Subfile: M - Mineral; I - Inorganic.
If there is a third symbol (=X), the compound does not satisfy chemistry.
+ - Identified Phases.

Figure 10. Philips computer printout for sample A-2

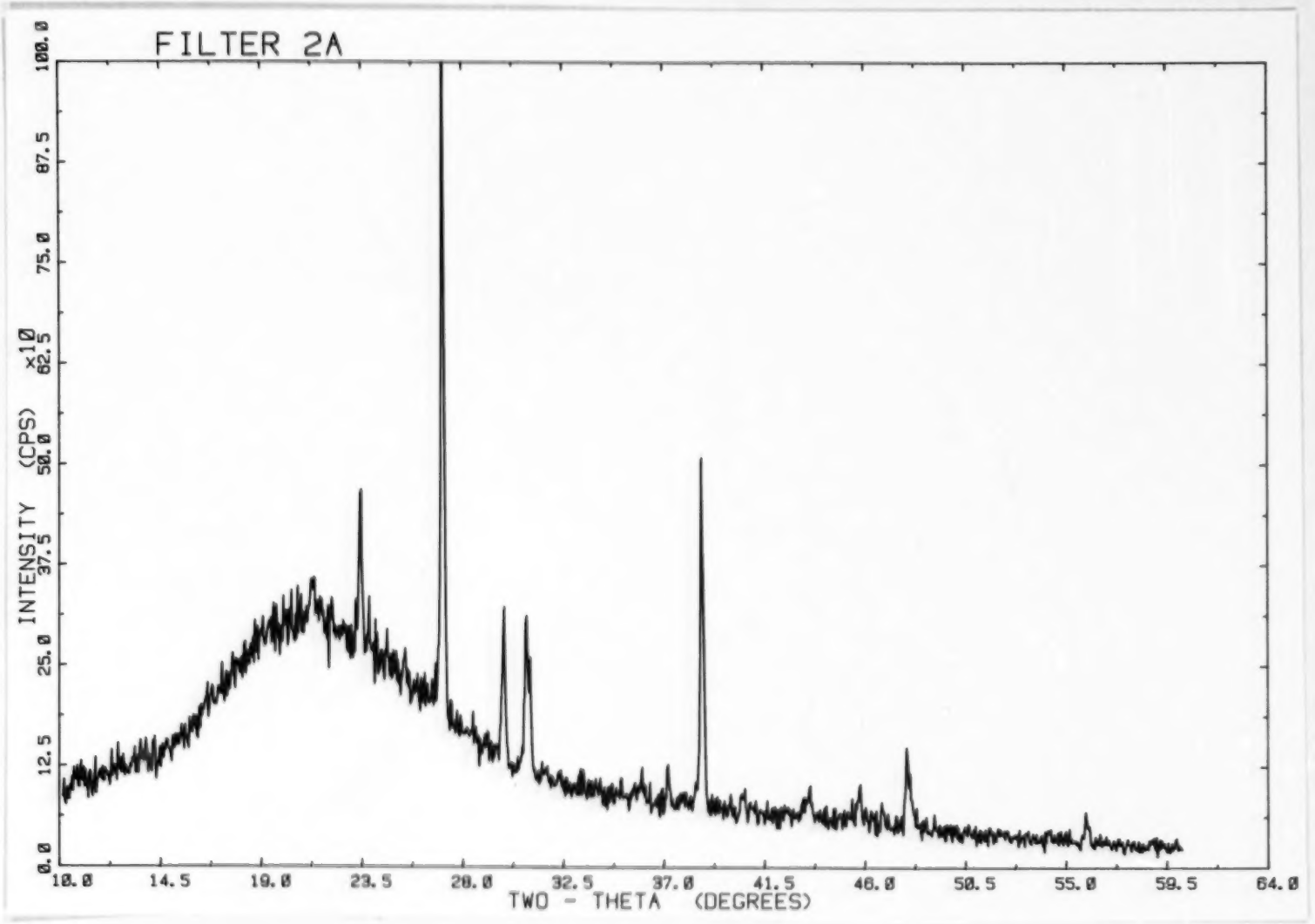



Figure 11. Siemens pattern of sample A-2

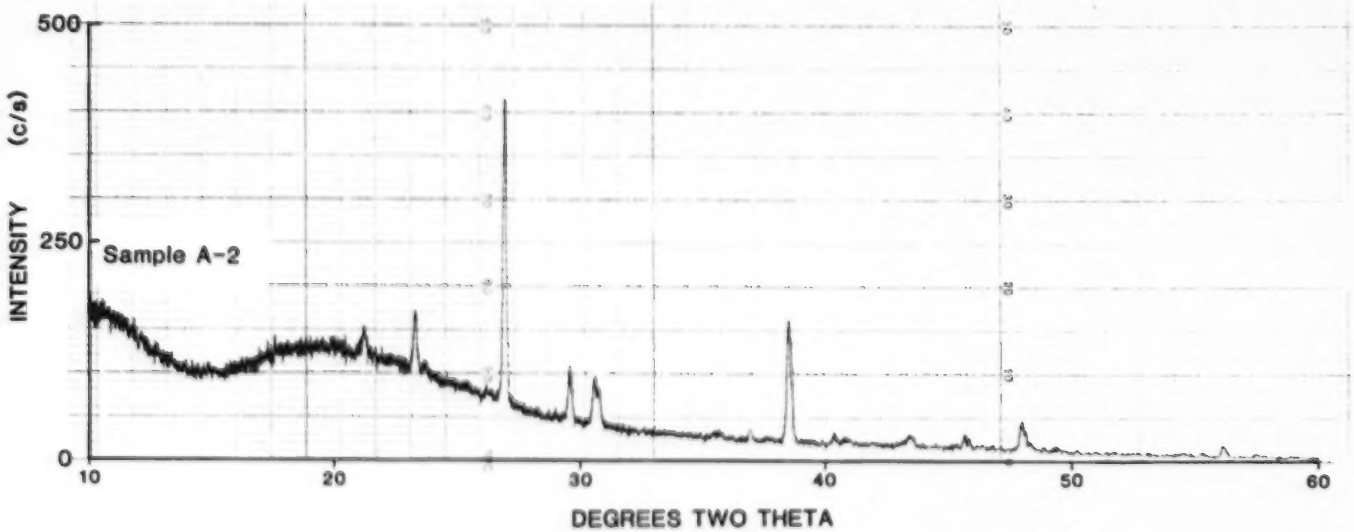



Figure 12. Diano pattern for sample A-2

tely enough to avoid the Al lines. At Siemens, $NH_4Cl$ was identified in B-3, but the same situation as with A-2 was observed: $K_2SO_4$ could only be indentified by entering the residual pattern manually. Conversely, at Rigaka only $K_2SO_4$ was identified in B-5; $NH_4Cl$ could not be found at all. Both compounds were found by the Diano instrument in B-3 except that $K_2SO_4$ was identified as $K_{2-x}(NH_4)_xSO_4$ a rather ill-defined compound having a very similar diffraction pattern. Again, the JCPDS card number listing in numerical order made it difficult to be certain that those two compounds among the 78 positive identifications were the most likely.

Samples C-6 run at Philips gave a pattern very similar to that observed at NRL. The result of the "search-match" identified the sample as a single phase hydrated double sulfate of sodium and magnesium [$Na_{12}Mg_7(SO_4)_{13}\cdot 15H_2O$] rather than a two phase mixture of the individual sulfates. Figure 13 shows the Match Score Table.

```
SANDMAN:  MATCH SCORE TABLE - REV 1.00                    2/ 9/81  15:12:51
                                                          F6C.D1

SAMPLE ID:  F6C              MAJOR PHASE SEARCH
  SCAN NUMBER
 24  USER LINES                 8.3370  D  1.5400                BKGND =28.2
SCAN PARAM:    45 KV  40MA  10.00 - 60.00 DEG  0.02 STEP     1.0 SEC/STEP
 23  LINES SEARCHED WITH  I  10.0          59 SEC SEARCH     35 SEC MATCH
25867   INITIAL PATTERNS            1053 INSPECTED              48  SCORED
 1  PHASES IDENTIFIED      AVE(EQ.D.E.) =  510 MICRONS       SCORE =  18.6
MATCH SCORE TABLE CONTAINS TOP  47 ENTRIES OF    47 ABOVE SEARCH CUTOFF


    MLMS   AMS   HT/MS/BK/UM  EQ.D.E.  I%    JCPDS#  DM   FORMULA
    ----   ---   -- -- -- --  -------  --    ------  --   -------

 1  15.3  18.6  23  0 48  3    510    138  + 29-1241  *M   NA12 MG7 ( S O4 )13*15 H2O
 2   8.8  -4.3  15  0 13  2    495    105    21-1139  DM   NA12 MG7 ( S O4 )13*15 H2O
 4   2.5  -1.1  13  0 17 50    345     68    19-1180  IM   NA AL SI2 O6 * H2O
 6   2.2  -3.4  13  1 21 16    405     59     7- 363  IM   NA AL ( SI O3 )2 * H2O
```

Figure 13. Philips Match-Score Table for Sample C-6

The MLMS and AMS values listed indicate an unambiguous identification of that double sulfate. The pattern could not be found in the manual search at NRL because the card was in Set 29 (issued 1979) which was not available. Siemens failed to identify sample C-4 for the same reason; set 29 was <u>not yet included</u> in their data file. Rigaku did have set 29 and succeeded in identifying the double salt in C-1 as indicated by the high R (for Reliability) factor shown on Fig. 14, the computer print out.

```
**********************************************************************************
*                                                                                *
*   RIGAKU/USA  X-RAY POWDER DIFFRACTION PATTERN SEARCH AND MATCH SYSTEM         *
*                                                                                *
**********************************************************************************


INPUT FILE NAME FOR PEAKS DATA:  Z00060.PK1
INPUT FILE NAME FOR PEAKS DATA:

SAMPLE:  FILTER 1C                                  PEAKS:  02-APR-8110:08:56

        THE   4 PATTERNS WITH THE HIGHEST RELIABILITY FACTOR

     JCPDS      M/MS    GX    I% EL  R     NAME

 1: 29-1241     7/ 9    78    90 *  492   SODIUM MAGNESIUM SULFATE HYDRATE / LOEWEIT
                                           E SYN
 2: 29- 797     2/10    20    74 *   89   LITHIUM AMMONIUM SULFATE
 3: 29- 796     2/10    20    73 *   88   LITHIUM AMMONIUM SULFATE
 4: 29-1158     1/ 8    33    27 *   60   SODIUM ACETATE
```

Figure 14. Rigaku computer printout for sample C-1

The Diano instrument recorded 23 peaks in the diffraction pattern of C-4 but failed to identify the compound among the 86 possibles (set 29 <u>was</u> included on Diano's data base).

During all these meaurements, failure to successfully identify the samples obviously mitigated against attempting a lower mass-loading from the same set. For those few cases where the run was a resounding success, a lower concentration sample was attempted. However, no success was achieved worth noting. At least a hundred micrograms per square centimeter seemed to be the mininum mass-loading that offered any chance of success.

Although this part of the exercise was not intended to address the problem of quantitative analysis but rather to establish the feasibility of qualitative identification, it is possible to make some estimates of the detection limits which might be achieved if the compounds present were known and if the strongest line of the compound of interest was free of interference. Take, for example, the Siemens run on Sample A-2 illustrated in Figure 11. The peak at about 27° 2θ is the strongest peak for KBr. Assuming that the sample is about 50% KBr and that counting times for the peak and background were each 100 seconds, the three sigma detection limit is calculated to be 0.4 $\mu g/cm^2$. The same assumptions for the NRL run of sample A-3 lead to a detection limit of 1.5 $\mu g/cm^2$. These values should not be taken too seriously, however, because of all the caveats that apply.

The mixture of four crystalline compounds without starch as a diluent (Mix III) listed in Table 2, was run at all four laboratories. Philips and Siemens identified all four compounds, Rigaku found three (missing $Al_2O_3$) and Diano could only identify two, $CaCO_3$ and $TiO_2$. Fig. 15 shows the video representation of the

Philips pattern and the Siemens X-Y recorder plot. Due to the press of time at Diano, a Mix I sample diluted with starch was left to be run at a later time. Philips actually identified all four of the compounds in Mix I (3% of each) although the computer print out did not recognize $Al_2O_3$ as being present by showing a "+" sign (see Fig. 10 for the meaning of the symbols); $Al_2O_3$ did show positive values in the "MLMS" and "AMS" columns. Siemens identified three of the compounds, missing $Al_2O_3$, although four of the strongest lines in the residual pattern were good matches for $Al_2O_3$. On the Rigaku instrument, three of the compounds were identified in Mix I; curiously, in this dilute sample, $Al_2O_3$ was found but $Fe_2O_3$ was not, in contrast to the Rigaku run on Mix III. The Diano run found 108 peaks in the diffraction pattern of Mix I which then proposed 107 possible compounds, none of which included the compounds known to be present.

Rigaku manufactures a rotating anode x-ray tube capable of operating at 12 kW. This x-ray tube was not in operation with the diffractometer at the time of the visit the their appplications laboratory. A sample of Mix I was left with them which was run later. Figure 16 shows continous scans of the diffraction pattern of that sample contrasting the results from the rotating anode tube with those using the standard x-ray tube. The increased intensity and smoother background with the rotating anode is quite obvious.

Diano has a high intensity x-ray system under development. It will be capable of operating up to 2.7KW but was not yet available when these samples were run. It should be capable of achieving intensities more than twice those realized during these measurements

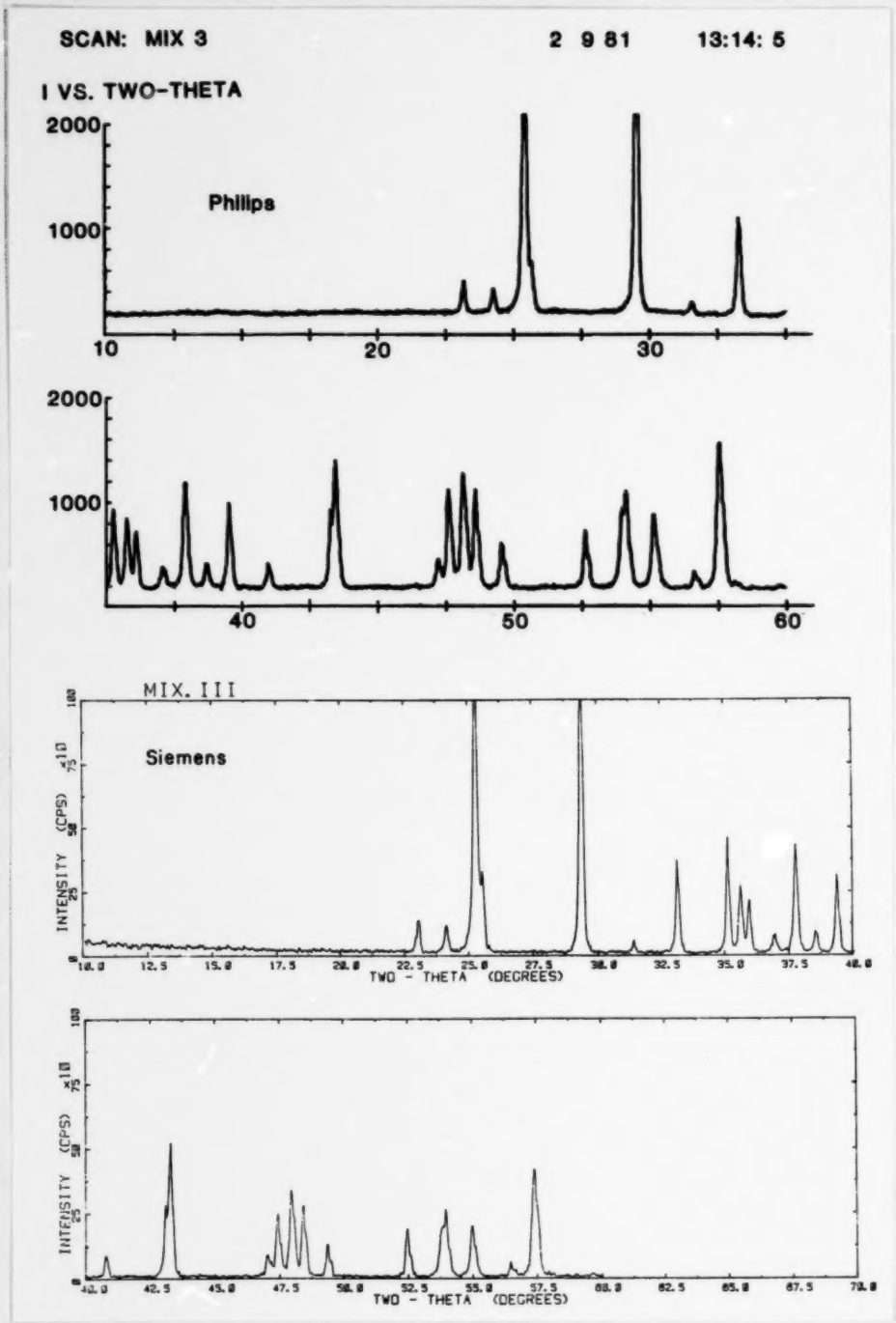



Figure 15. Mix III: Upper - Philips video presentation, Lower - Siemens X-Y plot.

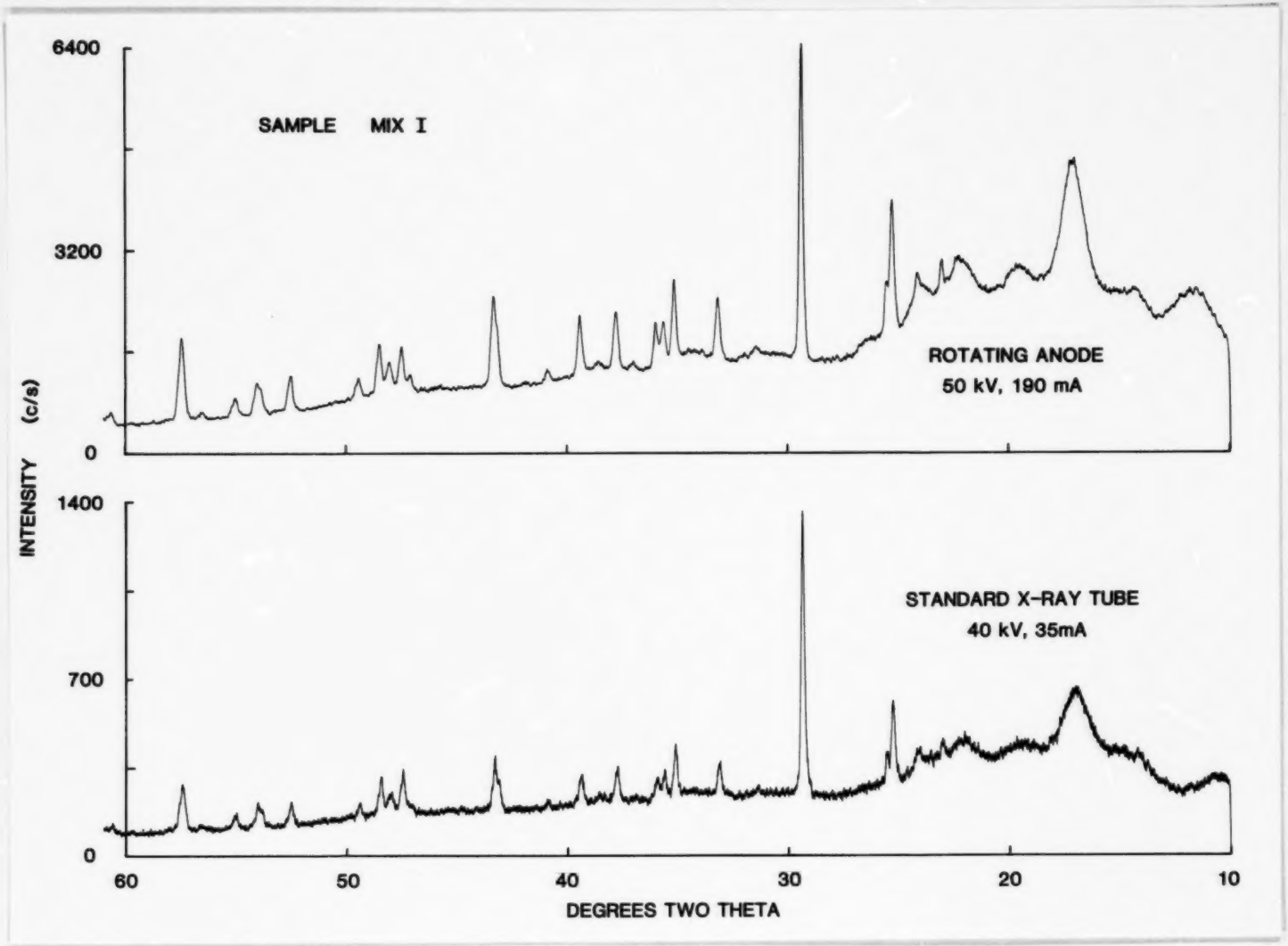



Figure 16. Rigaku scans of the diffraction pattern of Mix I.

with their instrument and thereby improve the chances of identifying low level concentrations.

The actual samples did not fare much better at the manufacturers' laboratories than they did at NRL. The bulk fly ash sample was identified as a mixture of three compounds, $Al_6Si_2O_{13}$, $SiO_2$ and $LiFe_5O_8$ at Philips, with some indication that $Fe_2O_3$ might be present. Siemens identified only one phase, $Fe_3O_4$, with a very large residual pattern. On visual inspection it seems likely that part of the residual pattern could match $Fe_2O_3$. The search-match at Rigaku resulted in a large number of probables, more than 50 (the Rigaku program prints out only the 50 possibilities with the highest reliability factor). The top few included $\beta$-$SiO_2$, $Fe_2O_3$, $AlSi_2O_6(OH)_2$, $Al_6Si_2O_{13}$ and a variety of other aluminosilicates, all of which seemed reasonable and consistent with the qualitative elemental information. However, also in the top group were such unlikely phases as $CeFe_2$ (no Ce detected by XRF), $\delta$-$(Fe_{.67}Mn_{.33})OOH$ (no Mn) and $(Ni,Zn)O.Fe_2O_3$ (no Ni or Zn). At Diano the fly ash pattern consisted of 38 peaks. From these, 54 possible compounds were identified. In this case a second "search-match" run was implemented, utilizing the qualitative elemental composition listed in Table 3. The number of possible identifications was reduced to 24, including such likely compounds as $MgAl_8Ti_6O_{25}$, low quartz ($SiO_2$), $Al_2SiO_5$, $\alpha$-$SiO_2$, $Fe_2O_3$ and $Fe_3O_4$, but also including such unlikely compounds as $CuSiO_3 \cdot 2H_2O$ (no Cu), $Mn_3O_4$ (no Mn), $Be_{17}Ta_2$ (no Ta) and $Pr_4Te_7$ (no Pr or Te).

The zinc smelter sample on a filter (NZC-10) was identified at Philips as $CaFe_4O_7$ although a comparison with the JCPDS card made

that identification suspicious. The Siemens run resulted in a good match for $(NH_4)_2SO_4$, quite reasonable for a sample in which S is the only element above atomic number 11 present in a major amount. The residual pattern consisted of only five lines and these were all lines which matched the $(NH_4)_2SO_4$ pattern but where the relative intensity was wrong, implying perhaps a preferred orientation problem. This sample wa not run at Rigaku. At Diano 41 peaks were identified in NZC-5. Of 41 patterns "matched" the only result satisfying chemistry was $(NH_4NSO_2)_3$-ammonium sulfonylimide, not a very likely compound.

SJA-15, a filter sample from the lead smelter, gave a diffraction pattern at Philips which matched a mixture of $NH_4SCN$ and $Pb_2Cl_3(OH)$. In a full 30 minutes of searching at Siemens, on a pattern which contained 22 lines, no match whatever could be found. SJA-16, run at Rigaku and Diano, could not identified at either laboratory, Only five peaks were found in the Rigaku pattern while over 100 were identified at Diano.

In does seem obvious from all of these measurements that the automated x-ray diffractometers operate marginally well when presented with reasonable samples but that, for the most part, pollution particulates collected on filters or in bulk make a less-than-ideal sample. It seems obvious also that these automated instruments must be attended by operators who can make judgements and do some manual manipulation of the data, as evidenced by the necessity to manually substract the other compound from the patterns for samples A-2 and B-3 in order to identify $K_2SO_4$ in those samples at Siemens. Further development should improve this situation.

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